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Contents

Mercury In the Estuary

by Rainer Hoenicke, Jay Davis, and Adrienne Yang

Mercury (or quicksilver) is a naturally occurring metal which has several forms. It is also one of the most toxic substances, especially when combined with other elements to produce organic mercury compounds like methylmercury. Mercury has been found throughout the San Francisco Estuary at elevated concentrations in water, sediment, and organisms. It is of particular concern as a human health issue, as it accumulates in tissues and its levels increase up the food web. For example, fish bioaccumulate mercury of the most toxic form--monomethylmercury--and fish at the top of the food web can harbor mercury concentrations over one million times the mercury concentration in the water in which they swim.

As a result of the tremendous increase in mercury production and use in this century, as well as the ease with which many forms of mercury dissolve in water, contamination of this metal is virtually world-wide. It travels easily through different environmental media including the atmosphere, in a variety of chemical forms, and is toxic to humans and other organisms in very low concentrations. California is unique in mercury contamination because in addition to the general, industrially related global increases, it also contains specific contamination sites. The California Coast Range contains one of the world's great geologic deposits of mercury. This mercury was mined intensively during the late 1800s and early 1900s primarily in support of gold mining in the Sierra Nevada where the mercury was used in the gold extraction process. A legacy of leaking Coast Range mercury mines and lost Sierra Nevada quicksilver is providing a significant, ongoing burden of mercury to the Estuary from both sides of the State (see also *Estuary*, Vol. 5, No. 5, October 1996, available from the San Francisco Estuary Project (510) 286-4392).

Toxicity and Health Concerns

As mercury cycles through various forms and media, its bioavailability (ability to contaminate organisms) and toxicity change. Toxicity heavily depends upon the form the mercury is in. Since only 2% of the intake of inorganic forms of mercury is estimated to be absorbed into the bloodstream, inorganic mercury such as mercury chloride (Hg_2Cl_2) is, relatively speaking, a minor health hazard and has, for a long time, been used in medicines as a purgative and in dental fillings. Other inorganic forms have long been known to be a health hazard. For example, mercury nitrate, $Hg(NO_3)_2$, was used during the Industrial Revolution to soften felt and caused twitching and dementia among hatters, giving birth to the phrase"mad as a hatter."

"In comparison, organic mercury forms such as methylmercury (CH_3Hg) and other organo-mercury compounds are much more toxic to humans, since over 90% of the intake of methylmercury, for example, is absorbed into the bloodstream.

Because mercury is found throughout the environment, everyone is exposed to low levels through inhalation, absorption, and ingestion. Long-term exposure to low levels of metallic mercury and organic mercury affects the nervous system. Long-term exposure to low levels of inorganic mercury affects the kidneys. Short term exposure to higher levels of any form of mercury can result in damage to the brain, kidneys, and fetuses. Mercury has been found to have a harmful effect upon a wide range of systems including the respiratory, cardiovascular, hematologic, immune, and reproductive systems.

Where Does Mercury Come From?

Natural Sources

Since mercury occurs naturally in the environment, there is a background concentration independent of human-related sources. Mercury can occur naturally in a variety of forms such as Hg^0 (elemental mercury), Hg^{+2} (dissolved in rainwater), or as the ore cinnabar HgS, and as an organo-metal, such as methylmercury. Through natural chemical and biological reactions, mercury changes form, becoming alternately more or less soluble in water, more or less toxic, and more or less biologically available.

As with any site on Earth, there is natural mercury contamination in San Francisco Bay. However, it is difficult to determine just what proportion of mercury in the Bay Area is from natural sources since what is natural varies from one part of the world to the next. Natural sources include volcanic activity, forest fires, and oceanic releases.

Human Sources

Mercury is used in a wide range of over 2,000 manufacturing industries and products including barometers, thermometers, mercury arc lamps, switches, fluorescent lamps, mirrors, catalysts for the oxidation of organic compounds, gold and silver extraction from ores, rectifiers, cathodes in electrolysis/electroanalysis, in the generation of chlorine and caustic paper processing, batteries, dental amalgams, as a laboratory reagent, lubricants, caulks and coatings, in pharmaceuticals as a slimicide, in dyes, wood preservatives, floor wax, furniture polish, fabric softeners, and chlorine bleach. Individual industries use different forms of mercury as well.

It is estimated that the net domestic annual use of mercury was about 3,409 tons in 1986. Of this use:

- 50% to 56% was used in the electrical industry,
- 12% to 25% was used in chlor-alkali plants to generate chlorine and caustic soda,
- 10% to 12% was used in paint manufacturing, and
- about 3% was used in the preparation of dental amalgams.

Global human-related sources include: coal-fired power plants, gasoline and oil combustion, smelting, chlor-alkali plants, sewage treatment, and mercury dumping from naval vessels. In the Bay Area much of the mercury contamination is due to mining related activities.

The Mining Connection

Historically, mercury was mined intensively in the Coast Range and transported across the Central Valley for use in Sierra Nevada placer gold mining operations. Virtually all of the quicksilver used in these operations was ultimately lost into Sierran watersheds. It has been estimated that, in river drainages of the Mother Lode region alone, approximately 7,600 tons of refined quicksilver was inadvertently deposited in conjunction with Gold Rush era mining. Additional mercury was used throughout the gold mining belt of the northwestern and central Sierra Nevada. The majority of Coast Range mercury mines which supplied this practice have since been abandoned and remain unreclaimed. As a result of these two activities, widespread mercury contamination exists today on both sides of the Central Valley.

Recent water quality data indicate that a significant amount of mercury from the Gold Rush era still exists in the sediment of the upper Yuba River watershed, and the mercury is being transported into Englebright Reservoir where it is largely trapped. Bioavailability studies show that the reservoir is acting as an interceptor of inorganic and methylmercury. Even though elevated levels of mercury are found in mined upstream tributaries and within the reservoir, the organisms below the catchment consistently show reduced mercury concentrations compared to above the reservoir. This means that the reservoir is acting as an interceptor of bioavailable mercury, preventing it from being transported downstream to the Estuary. Therefore much, but not all, of the mercury remaining from historic gold mining may be prevented from reaching the Estuary. However, in the rivers without dams, like the Cosumnes, gold mining mercury is still transported unimpeded to the Estuary.

Recent work also suggests that the Coast Range may be a more important source of mercury to Central Valley Rivers and the Estuary than the Sierra Nevada. Possibly due to the reservoir trapping effect, the export of mercury from northwestern Sierra Nevada rivers was found to be considerably less than that contributed from rivers in the north central and northwestern parts of the State.

As highlighted in *Estuary* (Vol. 5, No. 5, October 1996), highly elevated concentrations of mercury were observed in the Yolo Bypass during the unusually wet spring of 1995. Cache Creek, which drains Clear Lake, was determined to be a significant source of mercury. The areas draining Cache Creek have many large abandoned mercury mines, and are known to be enriched in mercury. Work by UC Davis researcher Darell Slotton on Davis Creek, a small tributary, has documented in-stream loads of approximately 200 kg of mercury in single wet seasons. Although mercury from Davis Creek is currently being intercepted by the Davis Creek Reservoir, mercury from other similar mercury mine regions remains available for downstream transport. Follow-up studies are underway by the Central Valley Regional Water Quality Control Board and Slotton to determine whether mines are the main source of mercury and to determine how the bioavailability of mercury varies throughout the watershed.

Data Trends in the Regional Monitoring Program

One of the apparently striking conclusions that can be drawn from RMP data is the lack of bioaccumulation of mercury in the bivalves transplanted for 90 to 100 days at various locations in the Bay for any of the three years of the RMP analyzed so far. Bivalves generally do not accumulate dramatically elevated mercury concentrations, and the mercury they do contain (primarily inorganic mercury) is transferred to the consumers of the bivalves far less efficiently than methylmercury.

Of more importance in consumption-related toxicity to humans is the pathway of methylmercury through larger fish that feed on other fish. Mercury bioaccumulation in these larger fish has resulted in tissue concentrations 100,000 times higher than concentrations in adjacent water. In 1994 a fish tissue contamination study was conducted for the San Francisco Estuary as part of the Bay Protection and Toxic Cleanup Program. Findings revealed tissue mercury concentrations above levels of human health concern in several fish species analyzed. Mercury concentrations were particularly high in the two shark species sampled. Based on the concentrations of mercury and other contaminants measured in this study, advisories concerning consumption of fish caught from the Bay were issued by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) in December 1994. Adults were advised to limit consumption of Bay sport fish to two meals per month. Pregnant or nursing women and children under six were advised to limit consumption to one meal per month. The advisory also states that large shark and striped bass should not be consumed at all. It should be noted that the advisory does not apply to salmon, anchovies, herring, and smelt caught in the Bay.

In 1997 a follow-up to the 1994 work is being conducted as part of the RMP. Seven species have been targeted for sampling, including striped bass, leopard shark, California halibut, white sturgeon, white croaker, shiner surfperch, and jacksmelt. The objectives of this sampling effort are:

1. to produce the information needed for updating human health advisories and conducting human health risk assessments, and
2. to measure contaminant levels in fish species over time to track trends and to evaluate the effectiveness of management efforts.

This sampling will be conducted in June. In order to establish long-term trends in concentrations, sampling for mercury and other contaminants in fish tissue will continue to be conducted in future years. For more information on RMP fish studies contact Jay Davis at SFEI: (510) 231-9539.

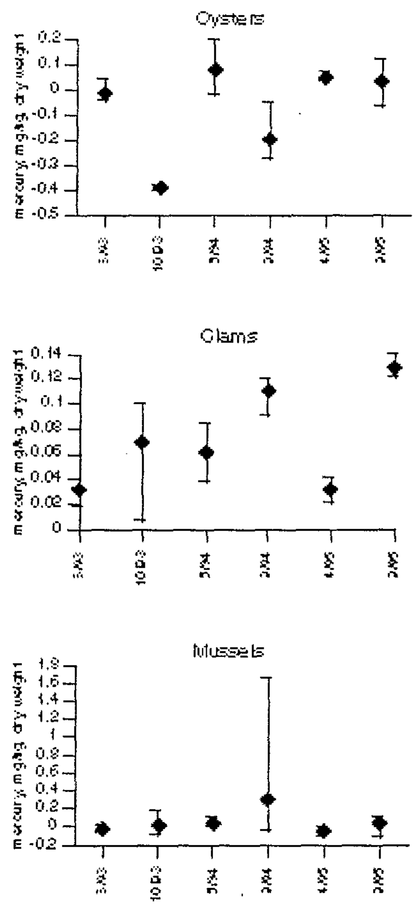

Figure 1. Mercury accumulation or depuration in three species of transplanted bivalves for six sampling periods from 1993-1995. Initial (T-0) concentrations are subtracted from tissue concentrations after retrieval to give concentrations accumulated or depurated (negative

value) during deployment in the Estuary. Bars indicate the range of values of all stations where species were deployed.

Potential Control Measures

Control of human-related sources of mercury pollution involves both point and area source control. Point source control is often wielded through mechanical or chemical means, while area control is often executed by administrative means. It is always true that it is easier to recover mercury at the source, where it is more concentrated, than it is to recover it after it has dispersed in different forms and species throughout the environment. The continuous cycling of mercury through its many different forms also complicates the job of devising effective clean-up methods.

Source Control: Mercury point source investigators have been very effective in isolating sources in the environment. Extremely sensitive analytical instrumentation is now available to monitor total mercury emissions or to analyze mercury's different forms down to the picogram (a millionth of a millionth of a gram) level. Source control includes the remediation of abandoned mines, waste stream capture, and flue gas scrubbing.

Area Control: Ingestion of fish and other seafood contaminated with methylmercury is a dominant source of mercury exposure in many parts of the United States and the world. Administrative controls to limit the exposure of humans to mercury include warning limits on the amount of fish consumed in a given period. Other area controls include capping waste sites to limit exposure to the environment, specialized dredging, and washing of mercury-contaminated soil and sediment.

The Regional Water Quality Control Board (Regional Board) has formed a task force to take a broad view of the mercury situation in the Northern Estuary from the Central Bay up to the Delta. The need for this pilot project surfaced because of smaller, shallow water. North Bay dischargers who are faced with regulation compliance problems if mercury limits were set at the same levels for all dischargers. The goal of this project is to find a broad range of cost-effective solutions for point and non-point source pollution and to determine the largest source(s) of mercury.

Key questions which will be considered by the Regional Board are:

- How does mercury get transported down a watershed system and where are the key points during the transport at which inorganic mercury is transformed to organic mercury, which poses a risk for the Estuary?
- What is the proportion of historic mercury contamination versus current sources?
- What is the rate at which existing sinks of mercury are moving from the Bay to the ocean and how do current loading rates affect this process?
- What human activities accelerate or dampen the transfer of mercury currently found in the Bay system to more bioavailable organic forms, and do the cumulative effects of these activities substantially increase human health and wildlife risks?
- How do we estimate mercury loading from the atmosphere, small North Bay watersheds, the Sacramento River, and point source discharges?

In the San Francisco Estuary, mercury contamination is probably far too widespread for direct or physical area control measures to be effective or economically feasible. However, significant opportunities may exist for effective point source remediation of important mercury discharges, which would otherwise continue to be transported into the Estuary.

Acknowledgments

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For more information on fish contamination in California, contact the Pesticide and Environmental Toxicology Section (PETS) of OEHHA, 2151 Berkeley Way, Berkeley, CA 94704-1011, at (510) 540-3063, or the Sacramento office, 601 North 7th Street, P.O. Box 942732, Sacramento, CA 94234-7320, at (916) 327-7319. County departments of environmental health may have more information on specific fishing areas.

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In Brief: 1995 RMP Results

by Adrienne Yang

The 1995 RMP Annual Report has been completed. That report includes monitoring results from the Base Program, Pilot and Special Studies, and summary and perspective articles contributed by RMP investigators and other scientists. Below are a few highlights from the RMP Base Program. For the Executive Summary and the full report please contact SFEI at (510) 231-9539 or visit our world wide web site at: http://www.sfei.org.

Water

Dissolved trace element (i.e., metals) concentrations were generally elevated at the Southern Slough and South Bay monitoring stations. Relative to other Estuary reaches, most dissolved trace organics were elevated in the South Bay with concentrations progressively decreasing from Coyote Creek to the Golden Gate station. This pattern was repeated with dissolved organics data adjusted for total suspended sediment, which indicated the presence of trace organic sources in the South Bay and DDT compounds at the Rivers station.

Clear seasonal variations were observed for arsenic, cadmium, dissolved silver, and some trace organics. Arsenic, cadmium, and dissolved PAH concentrations were high throughout the Estuary in August, silver concentrations were especially elevated in the South Bay in August, and the pesticide diazinon was highest at nearly all stations in February.

In 1995, the overall pattern of water quality exceedances was very similar to that of 1994: concentrations of many contaminants were above applicable water quality objectives or criteria. Of the trace elements, copper, chromium, lead, mercury, and nickel